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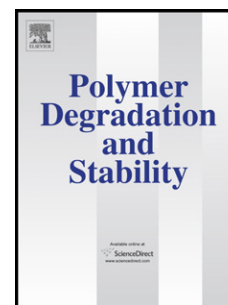
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## EFFECTS OF ALKALINE AND ACID SOLUTIONS ON GLASS/EPOXY COMPOSITES

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**Abstract** Composite structures can be exposed to a range of corrosive environments during their in-service life, which causes degradation in terms of material properties. The effect of alkaline and acid solutions on the GRP mechanical properties can be found in open literature, but the studies presented are not sufficient to establish a full knowledge of this subject. In this paper the flexural properties and the impact strength of a glass fibre/epoxy composite after immersion in hydrochloric acid (HCl) and sodium hydroxide (NaOH) were analyzed. Independently of the solution, the flexural strength and the flexural modulus decrease with the exposure time. However, alkaline solution promotes higher decrease of the flexural properties than the acid solution. The same tendency was observed for impact strength.

**Keywords:** Composites; Environmental Degradation; Failure; Hardness Measurement; Mechanical Characterization

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## 1 - Introduction

The interest in glass-reinforced plastics (GRP) components for highly corrosive environments, as an alternative to stainless or coated steel ones, is becoming common. They offer an attractive potential for reducing the weight, as consequence of their high specific strength and stiffness, competitive cost, good static and dynamic properties, good resistance to corrosion and simplified fabrication.

Nowadays, composite pipes are largely used in the chemical industry, building and infrastructures [1]. On the other hand the use of the GRP tanks in hydrometallurgical process plants or other components is becoming common [2]. However GRP tanks and pipes may be degraded due to abrasion, change in brittleness or hardness, delamination or separation of fibre from matrix and degradation of matrix due to high speed flow of hard particles, cyclic loading and unloading of tanks, diffusion of acid solutions and so on [2].

The effect of alkaline and acid solutions on the GRP mechanical properties can be found in open literature, but the studies presented are not sufficient to establish a full knowledge of this subject. Mahmoud *et al* [3] shows that the change in the flexural strength, hardness and Charpy impact resistance depends upon the type of acids and the period of immersion. For example, relatively to HCl, flexural strength was found to be insensitive until 30 days of immersion and, after this period, a decrease can be observed around 10%. In terms of hardness, they showed that the Barcol hardness of the polyester drops around 15% after 90 days of exposure. However, for external pipe surface the hardness was found to be insensitive until 30 days of immersion, while for internal surface this phenomenon was verified until 60 days. In terms of Charpy impact resistance a slight decrease, around 5%, can be observed until 60 days of immersion and in last 30 days (between 60 and 90 days) a significant drop of 10% occurs. Combining the HCl effect with

temperature, all properties above mentioned decreased significantly. Polyester and bisphenol A epoxy vinyl ester resins were exposed to two different acidic solutions (1M H<sub>2</sub>SO<sub>4</sub>, Co spent electrolyte), at two different temperatures (25 °C, 75 °C) and for two exposure durations (1 week, 4 weeks) by Banna *et al* [2]. They concluded that the polyester resin had lower modulus values when exposed to higher temperature solutions or higher exposure duration compared to the bisphenol A epoxy vinyl ester resin. For both resins the average hardness increased after 2 weeks of exposition and then decreased after 4 weeks exposure (but still higher than the unexposed). Finally, the microstructure of the polyester degraded more under acid and higher temperature exposure as indicated by increased surface roughness, cracks and diffusion of sulphur into the cracks. On the other hand, Stamenovic *et al* [1] studied the effect of alkaline and acid solutions on the tensile properties of glass-polyester composites. They concluded that the alkaline solution decreases the tensile properties (ultimate tensile strength and modulus) and this tendency increases with the pH value. Concerning the acid solutions, they increase the tensile properties and this tendency was more relevant when the pH value decreases. For both solutions, Stamenovic *et al* [1] concluded that the changes observed on the tensile properties are proportional with the exposure time (number of days in liquid). The effects of sulphuric acid concentration and the sequential layup of glass fibre reinforcements on the diffusion behaviour glass/epoxy laminates were studied by Pai *et al* [4]. The results showed that composite specimens with chopped strand mat as the skins layers exhibited higher weight gain than those with woven roving mat as the skin layers. Material degradation is more pronounced with the increase of sulphuric acid concentration, which can be explained by hydrolytic dissolving of the matrix in contact with this acid [1, 4]. Degradation studies were carried out in different solvents like 10% NaOH, 1 N HCl and 10% NaCl by Sindhu *et*

*al* [5] and its influence on mechanical properties was analyzed. It was observed that the tensile strength and the modulus (E) increases in acid environments and decreases for the other solvents. Finally, several studies were performed on GRP under stress corrosion cracking conditions [6-11]. According with Kawada and Srivastava [11] stress-corrosion cracking in GRP occurs as a result of a combination of loads and exposure to a corrosive environment. Sharp cracks initiate and propagate through the material as a direct consequence of the weakening of the glass fibres by the acid. The strength of the fibre reduces dramatically as a result of diffusion of acid and chemical attack of the fibre surface at the crack tip, which causes a highly planar fracture with a much reduced failure stress.

The aim of this work is study the flexural and low velocity impact response of a glass fibre/epoxy composite after immersion in hydrochloric acid (HCl) and sodium hydroxide (NaOH). Intends to increase the knowledge of the material degradation by two different solutions, an acid and an alkaline solution, in terms of flexural and impact strength. The bending test was selected because, according with Banna *et al* [2], is the most sensitive to the change of exposure conditions. On the other hand, impact damage is considered the primary cause of in-service delamination in composites, which are very dangerous because they have severe effects on the performance of those materials [12-17]. This subject, low velocity impact associated with highly corrosive environments, is not reported in bibliography yet and the low velocity impact is the most serious problem, given the difficulty of its visual detection [18, 19].

## **2 - Material and experimental procedure**

Composite laminates were prepared in the laboratory from glass fibre Prepreg

TEXIPREG<sup>®</sup> ET443 (EE190 ET443 Glass Fabric PREPREG from SEAL, Legnano, Italy) and processed in agreement with the manufacturer recommendations, using the autoclave/vacuum-bag moulding process. The laminates were manufactured with the stacking sequence  $[45_2, 90_2, -45_2, 0_2]_s$ . The processing setup consisted of several steps: make the hermetic bag and apply 0.05 MPa vacuum; heat up to 125° C at a 3-5° C/min rate; apply a pressure of 0.5 MPa when a temperature of 120-125° C is reached; maintaining pressure and temperature for 60 min; cool down to room temperature maintaining pressure and finally get the part out from the mould. The plates were manufactured in a useful size of 300x300x2.1 mm<sup>3</sup>.

The specimens used in the experiments were cut from these thin plates, using a diamond saw and a moving speed chosen to reduce the heat in the specimen. The static three point bending tests were performed using specimens cut nominally to 100x14x2.1 mm<sup>3</sup>. On the other hand, the samples used in the impact tests were cut from those thin plates to square specimens with 100 mm side and 2.1 mm thickness (100x100x2.1 mm<sup>3</sup>). Before corrosive exposure the impact samples were subjected to an impact of 8 J, by an impactor with diameter of 10 mm and mass of 3.4 kg.

The specimens were completely submerged into hydrochloric acid (HCl) and sodium hydroxide (NaOH). Both solutions presented a concentration of 10% in weight (wt.%) and the pH level is 13.0 and 1.5, respectively, for NaOH and HCl [20]. The exposure temperature was 25°C (room temperature) and the exposure durations were 12, 24 and 36 days. It is important to note that the both faces of composites were exposed to acid and alkaline environments, however, in real conditions only one face of composite structures is exposed. Afterwards, they were washed with clean water and dried at room temperature.

The bending tests were performed according to ASTM D790-2, using a Shimadzu AG-10 universal testing machine equipped with a 5kN load cell and TRAPEZIUM software at a displacement rate of 5 mm/min. All 3PB tests were also carried out at room temperature, with a span of 34 mm and, for each condition, 5 specimens were used.

Bending strength was calculated as the nominal stress at middle span section obtained using maximum value of the load. The nominal bending stress was calculated using:

$$\sigma = \frac{3PL}{2bh^2} \quad (1)$$

being P the load, L the span length, b the width and h the thickness of the specimen. The stiffness modulus was calculated by the linear elastic bending beams theory relationship

$$E = \frac{\Delta P \cdot L^3}{48\Delta u \cdot I} \quad (2)$$

where: I is the moment of inertia of the cross-section and  $\Delta P$  and  $\Delta u$  are, respectively, the load range and flexural displacement range at middle span for an interval in the linear region of the load versus displacement plot. The stiffness modulus was obtained by linear regression of the load-displacement curves considering the interval in the linear segment with a correlation factor greater than 95%.

The low velocity impact tests were made using a drop weight-testing machine Instron-Ceast 9340. An impactor with a diameter of 10 mm and mass of 3.4 kg was used. The tests were performed on circular section samples of 70 mm and the impactor stroke at the centre of the samples obtained by centrally supporting the 100x100 mm specimens. The

impact energy used for the first impact was 8 J, which corresponds to an impact velocity of  $2.16 \text{ ms}^{-1}$ . All the other multi impacts were performed using impact energy of 4 J, which corresponds to an impact velocity of  $1.53 \text{ ms}^{-1}$ . For each condition, five specimens were tested at room temperature. After impact tests, all the specimens were inspected in order to evaluate the size and shape of the delaminations. As the glass-laminated plates are translucent it is possible to obtain the image of the damage using photography. To achieve the best possible definition of the damaged area, the plates were photographed in counter-light using a powerful light source. Plates were framed in a window so that all the light could fall upon them.

In order to obtain the solvents absorption it was used the following procedure, in accordance with BS EN ISO 62:1999. The samples were placed in an oven at  $40^\circ\text{C}$  for 6 hours, then cooled and weighed in order to obtain the dry weight (DW). Afterwards, a series of samples were immersed in the respective solutions (HCl and NaOH) and periodically weighted to obtain the current wet weight (CWW). The water absorption in weight percentage (W%) was calculated from equation (3):

$$W\% = \frac{CWW - DW}{DW} \times 100 \quad (3)$$

After exposition to the corrosive environments, the roughness profiles were obtained by a Mitutoyo equipment, model SJ-500. In order to obtain the roughness parameters several measures were performed in different zones of all samples (relative to each condition). The surface topology was also observed in a scanning electron microscope (SEM). All specimens were sputtered coated with a 10 nm layer of gold prior to SEM observation. The morphology was evaluated using Philips XL30 equipment.



The hardness was evaluated by ultramicroindentation using Fisherscope H100 equipment and a load of 500 mN. The hardness values were corrected for the geometrical imperfections of the Vickers indenter, the thermal drift of the equipment and the uncertainty in the zero position according with reference [20]. The hardness,  $H$ , is defined as the maximum applied load during the indentation test,  $P_{\max}$ , divided by the contact area of the indentation immediately before unloading,  $A_C$ .

### 3 - Results and Discussion

#### 3.1 – Bending Loads

The material degradation, in terms of static properties, was analyzed by bending tests. Banna *et al* [2] studied the degradation of composite materials using tensile and bending tests and they concluded that the last one (bending tests) was the most sensitive to the change of exposure conditions. Figure 1 shows a representative example of the load versus flexural displacement curves for control samples and samples exposed at HCl and NaOH solutions during 36 days. These curves show, also, the typical behaviour observed for the other ones immersed during 12 and 24 days. Both curves illustrate a linear elastic behaviour, in an early stage, with a non-linear region that starts around 80 MPa. After peak the load decreases and the drop observed is similar in all curves, which reveals that the damage mechanisms are very close. Typical pictures of the failure mechanisms are presented in Figure 2, where the exposure time of 36 days is representative of the others ones. For all laminates, solutions and time of immersion the main damage observed occurs by the fibres fracture in the tensile surface followed by delaminations between the layers. These delaminations, independently of the solution, increases with the time of immersion

but, for all exposure duration studied, they are higher in alkaline solutions than in acid ones. Comparing Figure 2b and 2c is possible to observe that the failure mechanisms are very similar, however, the delamination's size is bigger for samples exposed to alkaline solutions (Figure 2b). The delamination's size was statistically verified on five samples tested, for each condition, and values around 6.1% higher were found for NaOH solution.

Five specimens were tested, for each condition, and the average values with the respective standard deviations are presented in Table 1. The bending strength is calculated as the maximum bending stress at middle span with the maximum loading obtained from the load-displacement plots (equation 1) and the bending stiffness modulus is calculated using equation (2). It is possible to observe that, independently of the solution, the flexural strength and the flexural modulus decreases with the exposure time. For sodium hydroxide (NaOH) the flexural strength decreases around 5.8%, 11.1% and 22% for 12, 24 and 36 days of exposure, respectively. Relatively to the hydrochloric acid solution (HCl) the flexural strength decreases, respectively for the same exposure time, around 2.9 %, 9.0% and 16.2%. Similar tendency was observed for the flexural modulus with values around 10.7%, 18.2% and 26.9% for sodium hydroxide (NaOH) and 12.1%, 17.8% and 22.3% for hydrochloric acid solution (HCl), respectively, for 12, 24 and 36 days of exposure duration. The obtained results lead to the conclusion that the alkaline solution promotes higher decrease of the flexural properties than the acid solution. In fact alkaline solutions are highly corrosives [1, 21] and, according studies developed by Stamenovic *et al* [1], the influences of alkaline solution on mechanical properties increase with the pH value. Finally, the discussion done before agrees with the literature [2, 3] but disagree with reference [1] where was observed a decrease of the tensile properties for alkaline solutions and an increase of these properties with acid solutions.

In order to explain this decrease of mechanical properties some additional tests were done. The absorption curves were obtained and Figure 3 shows the results obtained for the sodium hydroxide (NaOH) and hydrochloric acid (HCl). It is possible to observe a weight gain up to 36 days (864 hours), with values relatively close, and the same trend is expected after this value. Therefore, this absorption leads to matrix expansion, with the consequent occurrence of pits [22] and/or development of microstresses in the composites [23, 24].

The presence of micro-cracks was analyzed and Table 2 present the statistic of the roughness measurements, where is evident the effect of the solutions on surface topology and the exposure time. For example, in terms of  $R_z$  (average peak to valley height), it is possible to observe that roughness increase with the exposure time, 4.13 to 5.39  $\mu\text{m}$  for HCl and 5.18 to 5.79  $\mu\text{m}$  for NaOH, but after 36 days of exposure  $R_z$  is slightly higher (7.4%) for sodium hydroxide.

In order to confirm the findings obtained from roughness profile, the surface topology was observed in a scanning electron microscope (SEM). Figure 4 shows the typical pictures obtained, where it is possible to observe that the unexposed samples (control samples) are characterized by a smooth surface, Figure 4a, and when the exposure time increases the laminates present a significant increase of micro-cracks. Studies developed by Hammami and Al-Ghilani [22] show, for example, that the combined action of water and corrosive fluids leads to matrix expansion and the occurrence of pits. After longer immersion time occur blisters, which may start growing by swelling (pressure) until final collapse [22]. Therefore, it is evident that the smooth unexposed surface becomes rougher with the time exposure, which is according with Table 2 and Banna *et al* [2]. Comparing Figures 4d and 4g, it is possible to observe that the major damages occur for samples exposed to the sodium hydroxide (NaOH). For example, Figure 4d shows long

cracks and the fibres exposition (there are zones where the fibres are completely visible) as consequence of the matrix's dissolution by the solution (NaOH). On the other hand, in Figure 4g the fibres are not visible but, in terms of matrix, major damages occur. In this case, HCl promotes multiple cracks on the matrix.

Finally the hardness was evaluated by ultramicroindentation and Figure 5 shows the schematic representation of the typical load–penetration depth curves for control samples and laminates exposed to NaOH solution. These curves are representative of the load–penetration depth curves obtained for laminates immersed in HCl during 12, 24 and 36 days. It is possible to conclude that the curves are agreeing with other ones presented in the literature [20] and the important quantities in this loading–unloading cycle are maximum load, maximum depth, final depth after unloading and the slope of the upper portion of the unloading curve known as the elastic contact stiffness. According with Figure 5 it is possible to observe that the maximum depth occurs for control samples and, when the specimens are exposed to the NaOH solution, this value decreases. Higher time of immersion contributes for a slight decrease of the maximum depth. Table 3 presents the average values of hardness, indentation modulus ( $E_R$ ) and Young's modulus of the matrix. It is possible to conclude that the measured hardness of the polymeric matrix increases after immersion in both solutions, in comparison with the control samples ( $\approx 0.24$  GPa). The higher average value of hardness is achieved during the first stage of immersion, 12 days, leading to hardness increases of around 20.8 % for laminates immersed in NaOH and 12.5 % for laminates immersed in HCl. Higher exposure time, for both solutions, does not promote any significant change in terms of the matrix hardness values. This tendency agrees with Banna et al [2] where the similar tendency was observed. According with these authors the hardness increases for 1 week exposure but later decreases with time. Finally,

the indentation modulus ( $E_R$ ) and Young's modulus of the matrix was obtained according with Antunes *et al* [20], where the indentation modulus ( $E_R$ ) is a function of the Young's modulus ( $E$ ) and the Poisson ratio ( $\nu$ ) of the specimen and the indenter. It is possible to conclude that, for both solutions, these values ( $E_R$  and  $E$ ) decrease compared with the results obtained for control samples. The drop occurred in terms of Young's modulus promoted by the corrosive solutions, and exposure time, can explain the lower flexural properties associated with the matrix/fibre interface degradation.

All these analysis agree with the bibliography and explain the drops observed on mechanical properties with the exposure to aggressive solutions. Mahmoud *et al* [3], for example, associated the drop of mechanical properties with the absorption, penetration and reaction that occur between the solutions and the composite constituents (matrix and fibres). In terms of matrix, the solution penetrates through the resin and separates out in micro-cracks [11]. On the other hand, the degradation of the fibre/matrix interface is caused by the dehydration of the matrix and penetration of solutions through micro-cracks [1, 25], crazes or similar voids in the matrix [11]. For Hammami and Al-Ghilani [22] the degradation takes place via two stages. In the first stage resin is attacked under the combined action of water diffusion and the presence of  $H^+$ . In the second stage the fibre itself is attacked and cracks appear on the fibre surface. This affects significantly the composite resistance to loading stresses [22]. However, according with Stamenovic *et al* [1], the most significant influence is on the fibre-matrix connection where this influence promotes the weakness of the load carrying capacity of material. This conclusion explain clearly the damage mechanisms observed in Figure 2b and 2c where the larger delamination, relatively to the control samples, are consequence of the poor interface fibre/matrix promoted by the aggressive environments.

### 3.2 – Impact Loads

Low velocity impact events can occur in-service or during maintenance activities promoting various types of damages, which are very dangerous because they are not easily detected visually, but, affect significantly the residual properties [12-19]. In this context, intends to obtain the residual life (until full perforation) of laminates subjected to multi-impacts after a first impact with higher energy and how can be affected, the residual life, by the aggressive environments. For this purpose the laminates were pre-impacted with energy of 8 J, followed by multi-impacts of 4 J.

Figure 6 shows the typical load-time, load-displacement and energy-time curves for the first impact carried out with energy of 8 J and before corrosive exposure. These diagrams represent a typical behaviour and are in agreement with those reported on literature [26-29]. The load-time and load-displacement curves are characterized by an increasing of the load up to a maximum value,  $P_{\max}$ , followed by a drop after the peak load. In all tests the impactor sticks into specimens and rebound always, which means that the maximum impact energy was not high enough to infiltrate full penetration [29]. In terms of average values the maximum load ( $P_{\max}$ ), maximum displacement and impact time is, respectively, around 2636 N (St. Dev.  $\approx 49$  N), 4.73 mm (St. Dev.  $\approx 0.1$  mm) and 8.42 ms (St. Dev.  $\approx 0.2$  ms). From the curves that represent the evolution of the energy with time, the beginning of the plateau of the curve coincides with the loss of contact between the striker and the specimen. This energy coincides with that absorbed by the specimen and the elastic energy can be calculated as the difference between the absorbed energy and the energy at peak load [29]. For the present condition the elastic energy was around 22.5 % (St. Dev.  $\approx 1.54$  %). Finally, Figure 7 shows typical damages occurred on laminates after impact loads and the average damage size is around 398.9 mm<sup>2</sup> (St. Dev.  $\approx 21.4$  mm<sup>2</sup>). It is

possible to observe that the delamination shape is oriented on the fibres direction of the adjacent lower ply (45°) and the crack is also aligned with the fibres direction of this lowest ply. Some matrix cracking induced by shear can also be identified in the middle group of layers (90°/-45°), which demonstrates an interaction phenomenon between matrix cracking and delamination, thus constituting a complex damage mechanism. More details about the damages promoted by impact loads can be found in [30-31].

These pre-impacted laminates were divided into three groups, where two of them were immersed in HCl and NaOH solutions, and all specimens were subjected to impacts with energy of 4 J. The curves obtained are similar to those presented in Figure 6, but with different average values. Table 4 shows the effect of the aggressive environment and exposure time on maximum load ( $P_{\max}$ ), maximum displacement and elastic energy in terms of average values and respective standard deviation. As expected, for the control samples, practically all these results obtained for 4 J are lower than the values obtained for 8 J. It is possible to observe also that the corrosive environments present significant effects in load, displacement and contact time. For example, comparing the control samples with samples immersed on NaOH solution during 12 days, the load and contact time decrease around 18.5% and 7%, respectively, while the displacement increases around 37.1%. On the other hand, comparing the values obtained between control samples and samples immersed on HCl solution during 12 days, it was obtained decreases around 5.4% and 15.2% for load and contact time, respectively, while the displacement increases 39.7 %. The exposure time present a considerable effect, occurring decreases in terms of maximum load around 20.4% for NaOH and 8.2% for HCl, when compared the values obtained between 12 days and 36 days of exposition time. In terms of maximum displacement and contact time it was observed an increasing around 24.5% and 15.7%, respectively, for

NaOH solution. The same tendency was observed for HCl solution with an increasing of 12.1% and 9.9%, respectively.

Figure 8 shows the effect of the aggressive solutions, and exposure time, on elastic energy and damage area after first impact at 4 J. The elastic energy was calculated as the difference between the absorbed energy and the energy at peak load [29]. It is possible to observe that the elastic energy decreases when the samples are exposed to corrosive environments and this tendency shows be highly dependent with the exposition time. For example, a decrease of 12.6 % occurs for HCl solution and 26.5 % for NaOH solution when it is compared the exposition time between 12 and 36 days. As expected the damaged area increases with the decreasing of elastic energy. Comparing with the control samples, the samples immersed in HCl and NaOH solutions, during 36 days, present an increasing of the damaged areas around 20.8 % and 24.7 %, respectively. Therefore, the alkaline solution promotes more damaged area than observed for acid solution, because alkaline solutions are highly corrosives [1, 21], and this tendency agrees with the bending results presented in last section.

A more significant effect of NaOH compared to HCl on load, displacement, elastic energy and damage area was observed. In fact, according with Figure 4 and Table 2, the major damages occur for samples exposed to the sodium hydroxide (NaOH) and it is known that there is an interaction mechanism between matrix cracking and delamination for composite plates submitted to low velocity impact. This crack interacts with delamination, thus contributing to increase the damaged area (consequently the elastic energy decreases) [32]. On the other hand, according for Stamenovic *et al* [1], the poor fibre-matrix connection promotes the weakness of the load carrying capacity of material. An important effect of the defect size on the maximum force (which decreases with



increasing defect dimension) was found by Amaro *et al* [16] and the plate deflection is proportional to the bending stiffness [32].

According with David-West *et al* [33] the impact bending stiffness has been known as an important property to assess the damage resistance of a composite, in particular delaminations. The slope of the ascending section of the load-displacement plot is the bending stiffness, however, more details to determine this property can be found in [33]. Table 5 presents the impact bending stiffness, after first impact at 4 J, showing the effect of the corrosive environment and exposure time on the damage resistance. For both solutions, it is possible to observe that the impact bending stiffness decreases relatively to the value obtained for the control samples. The impact bending stiffness is also highly dependent of exposure time, according with the values presented in Table 5. Therefore, this analysis confirms the tendency observed on Figure 8, where the damaged area increases with the presence of corrosive solutions and time exposure.

The effect of multi impacts was studied and Table 6 shows the impact resistance for the different corrosive solutions and exposure time. The laminates were considered failed, when full perforation (FP) occurs. Full perforation (FP) is defined when the impactor completely moves through the samples. It is possible to observe that the resistance of the laminates to repeated low velocity impacts is very dependent of the corrosive environment and the exposure time. After 36 days of immersion, for example, the impact resistance decrease around 64.3 % for the sodium hydroxide solution (NaOH) and 35.7 % for the hydrochloric acid solution (HCl), when compared with the control samples. This tendency was expected, because the major damages occurred for the sodium hydroxide solution as consequence of its highly corrosive effect.

Figure 9 presents the evolution of the elastic energy with the impact number, where

the last impact it is not represented because occurs full penetration (Elastic energy = 0). As expected, the elastic energy decreases when the number of impacts increases and this tendency shows to be very dependent of the solution type and exposure time. A major decrease in terms of elastic energy occurs for specimens immersed in alkaline solutions. On the other hand, lower elastic energy means that the damage area is major and this relationship can be observed in Figure 10. From this figure, it is evident that the damaged area increases with the number of impacts (which agrees with Figure 9 in terms of lower elastic energy) and, this tendency, is inverse of the occurred for impact bending stiffness. Figure 11 shows, for example, the pictures that show the evolution of the damage with the impact numbers for specimens immersed on HCl solution. They are representative of the specimens immersed on NaOH solution. In terms of impact bending stiffness, Figure 10, the results agree with David-West *et al* [33] and prove that is an important property to assess the damage resistance of composites. In this context, following the procedures of continuum damage mechanics [34-36] a damage parameter can be proposed, according with the equation:

$$D = 1 - \frac{E_{ibs}^*}{E_{ibs}} \quad (4)$$

where  $E_{ibs}^*$  is the current impact bending stiffness and  $E_{ibs}$  the impact bending stiffness for undamaged specimen. It is expected that the limiting values of  $D$  are 0 (for undamaged material) and 1 (for failed material). Therefore, this parameter ( $D$ ) can be used to estimate the degradation level of the composite laminates subjected to impact loads.

#### 4 - Conclusions

This work studied the flexural and low velocity impact response of a glass fibre/epoxy composite after immersion in hydrochloric acid (HCl) and sodium hydroxide (NaOH).

It was concluded that the corrosive environment affects significantly the flexural strength and flexural modulus. The exposure time was determinant on the mechanical properties degradation. The alkaline solution shows to be more aggressive than the acid solution, promoting the lowest flexural properties. Complementary tests were carried and the ultramicroindentation shows a decrease of the matrix mechanical properties. The roughness increases with the exposure time and is higher for the samples immersed in NaOH solutions.

In terms of impact it was concluded that the resistance of the laminates to repeated low velocity impacts is very dependent of the corrosive environment and the exposure time. The alkaline solution shows to be more aggressive than the acid solution, promoting the lowest impact resistance. The maximum load decreases with the impact numbers, however, the contact time and displacement presents the inverse tendency. The elastic energy decreases also with the impact numbers and, consequently, the damaged area increases. The impact bending stiffness showed to be an important property to assess the damage resistance of composites.

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Table 1 - Effect of corrosive environment on bending properties.

Table 2 - Statistics of the roughness measurements.

Table 3 - Effect of corrosive environment on average values of hardness, indentation modulus and Young's modulus of the polymeric matrix.

Table 4 - Effect of corrosive environment and exposure time on laminates pre-impacted.

Table 5 - Impact bending stiffness after first impact at 4 J.

Table 6 - Impact resistance.

Table 1 - Effect of corrosive environment on bending properties.

<b>Samples</b>		<b>Aver. Flexural Stress [MPa]</b>	<b>Std. Dev. [MPa]</b>	<b>Aver. Flexural Modulus [GPa]</b>	<b>Std. Dev. [GPa]</b>
Control samples		416.04	2.84	20.548	1.75
NaOH	12 days	392.05	4.87	18.352	2.01
	24 days	369.96	6.71	16.816	2.47
	36 days	324.63	7.01	15.016	3.11
HCl	12 days	403.93	6.01	18.058	2.74
	24 days	378.02	7.14	16.894	5.01
	36 days	348.61	8.11	15.967	6.77



Table 2 - Statistics of the roughness measurements.

Statistic values [ $\mu\text{m}$ ]	Samples / Exposure time						
	Control samples			HCl			NaOH
		12 days	24 days	36 days	12 days	24 days	36 days
Arithmetic average, $R_a$	$0.97 \pm 0.04$	$1.07 \pm 0.04$	$1.10 \pm 0.05$	$1.24 \pm 0.04$	$1.05 \pm 0.05$	$1.28 \pm 0.06$	$1.40 \pm 0.04$
Root mean square, $R_q$	$1.18 \pm 0.05$	$1.28 \pm 0.05$	$1.39 \pm 0.05$	$1.54 \pm 0.04$	$1.33 \pm 0.05$	$1.58 \pm 0.05$	$1.73 \pm 0.06$
Average peak to valley height, $R_z$	$3.15 \pm 0.08$	$4.13 \pm 0.07$	$4.19 \pm 0.07$	$5.39 \pm 0.05$	$5.18 \pm 0.09$	$5.36 \pm 0.08$	$5.79 \pm 0.08$
Evaluation length, $L_o$	$0.80 \pm 0.01$	$2.50 \pm 0.01$	$2.51 \pm 0.01$	$2.50 \pm 0.01$	$2.50 \pm 0.01$	$2.50 \pm 0.01$	$2.51 \pm 0.01$
Core roughness depth, $R_k$	$3.57 \pm 0.08$	$3.14 \pm 0.05$	$3.61 \pm 0.06$	$3.42 \pm 0.04$	$3.12 \pm 0.07$	$4.55 \pm 0.08$	$4.25 \pm 0.08$
Reduced peak height, $R_{pk}$	$0.49 \pm 0.019$	$1.28 \pm 0.01$	$2.28 \pm 0.01$	$1.86 \pm 0.02$	$1.68 \pm 0.02$	$1.03 \pm 0.02$	$1.75 \pm 0.02$
Reduced valley depth, $R_{vk}$	$1.21 \pm 0.07$	$0.23 \pm 0.07$	$1.36 \pm 0.06$	$2.23 \pm 0.05$	$0.64 \pm 0.05$	$1.88 \pm 0.07$	$1.94 \pm 0.06$

Table 3 - Effect of corrosive environment on average values of hardness, indentation modulus and Young's modulus of the polymeric matrix.

Samples	Aver. Hardness VH [GPa]	Std. Dev. [GPa]	Aver. E <sub>R</sub> [MPa]	Std. Dev. [MPa]	Aver. E [GPa]	Std. Dev. [GPa]
Control samples	0.24	0.01	13.12	0.94	11.64	0.91
NaOH	12 days	0.29	0.01	9.3	0.44	8.23
	24 days	0.27	0.01	9.15	0.67	8.1
	36 days	0.28	0.01	8.7	0.64	7.7
HCl	12 days	0.27	0.01	7.6	0.2	6.73
	24 days	0.25	0.01	7.43	0.21	6.53
	36 days	0.26	0.01	7.1	0.57	6.25

Table 4 - Effect of corrosive environment and exposure time on laminates pre-impacted.

Samples	Aver. Maximum Load [N]	Std. Dev. [N]	Aver. Maximum Displacement [mm]	Std. Dev. [mm]	Aver. Contact Time [ms]	Std. Dev. [ms]
Control samples	2721.4	64.0	2.29	0.13	7.75	0.21
NaOH	12 days	2219.3	59.1	0.16	7.21	0.24
	24 days	2108.6	50.8	0.21	7.61	0.31
	36 days	1765.8	61.4	0.18	8.34	0.29
HCl	12 days	2573.7	45.1	0.14	6.57	0.19
	24 days	2439.2	68.7	0.17	6.79	0.26
	36 days	2362.6	60.3	0.12	7.22	0.13

Table 5 - Impact bending stiffness after first impact at 4 J.

Sample		Impact Bending stiffness [N/mm]	St Dev [N/mm]	Variation relatively to control samples [%]
Control		1435.7	48.9	
NaOH	12 days	1217.1	51.1	-15.2
	24 days	747.6	60.5	-47.9
	36 days	593.3	69.4	-58.7
HCl	12 days	1125.7	54.7	-21.6
	24 days	792.6	61.1	-44.8
	36 days	684.1	63.4	-52.4

Table 6 - Impact resistance.

Sample		Number of impacts to failure
Control		14
NaOH	12 days	11
	24 days	7
	36 days	5
HCl	12 days	10
	24 days	9
	36 days	9

## Figures

- Figure 1 - Typical load-displacement curves for control samples, HCl and NaOH samples immersed during 36 days.
- Figure 2 - Failure mechanisms: a) Control samples; b) Samples exposed to NaOH during 36 days; c) Samples exposed to HCl during 36 days.
- Figure 3 - Weight gain versus exposure duration.
- Figure 4 - SEM pictures for: a) Control samples, b) Samples exposed to NaOH during 12 days; c) Samples exposed to NaOH during 24 days; d) Samples exposed to NaOH during 36 days
- Figure 5 - Schematic representation of the typical load-penetration depth curves.
- Figure 6 - Typical load-time, load-displacement and energy-time curves for laminates impacted at 8 J before corrosive exposure.
- Figure 7 - Typical picture of the damaged laminates impacted at 8 J.
- Figure 8 - Effect of the aggressive solutions on elastic energy and damage area after first impact at 4 J.
- Figure 9 - Evolution of the elastic energy with the impact numbers for: a) Samples exposed to HCl; b) Samples exposed to NaOH.
- Figure 10 - Evolution of the damage area and impact bending stiffness with the impact numbers for: a) Samples exposed to HCl; b) Samples exposed to NaOH.
- Figure 11 - Typical damages occurred for samples immersed on HCl during 36 days: (a) 2<sup>nd</sup> Impact; (b) 5<sup>th</sup> Impact; (c) 8<sup>th</sup> Impact.

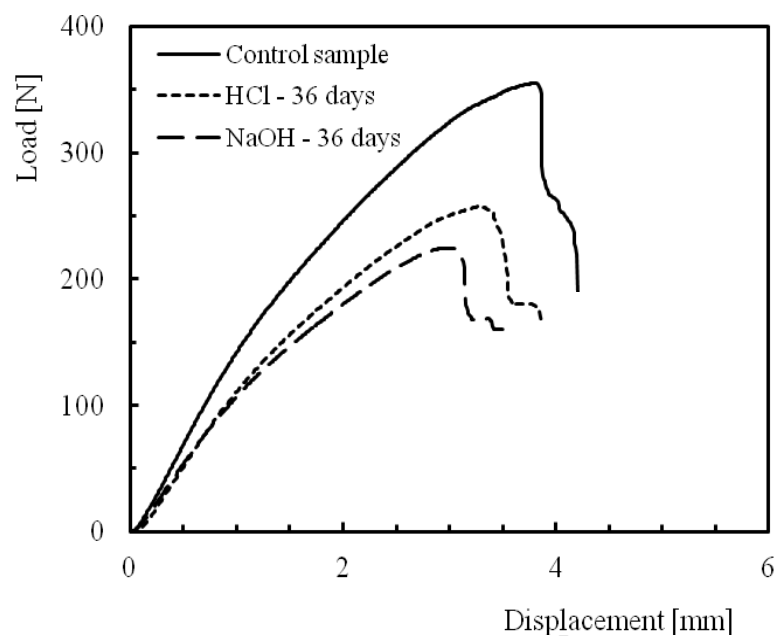


Figure 1 - Typical load-displacement curves for control samples, HCl and NaOH samples immersed during 36 days.

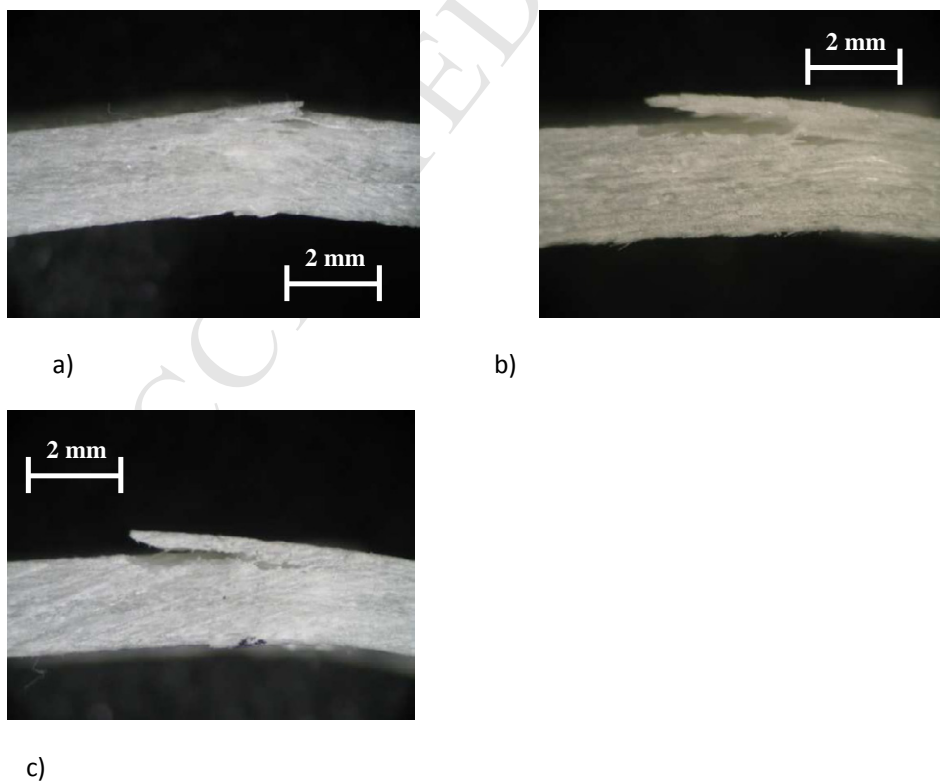


Figure 2 - Failure mechanisms: a) Control samples; b) Samples exposed to NaOH during 36 days; c) Samples exposed to HCl during 36 days.

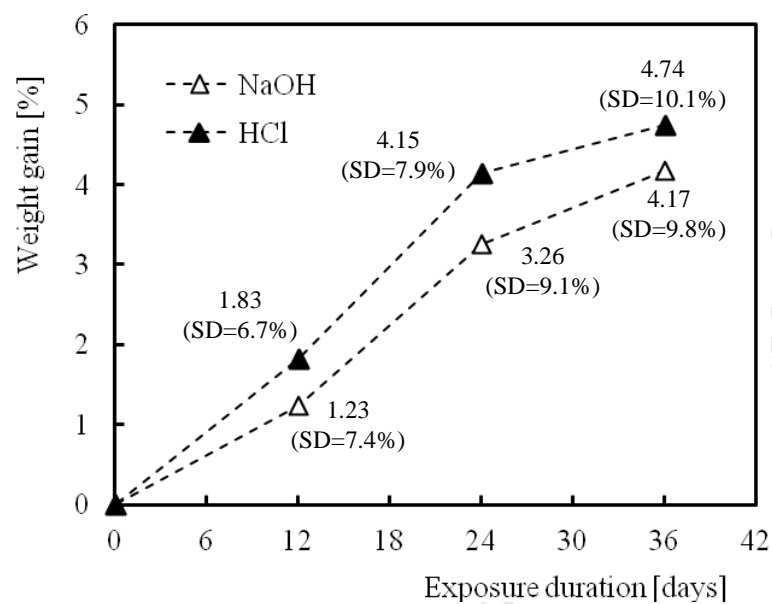


Figure 3 – Weight gain versus exposure duration (SD=Standard Deviation).

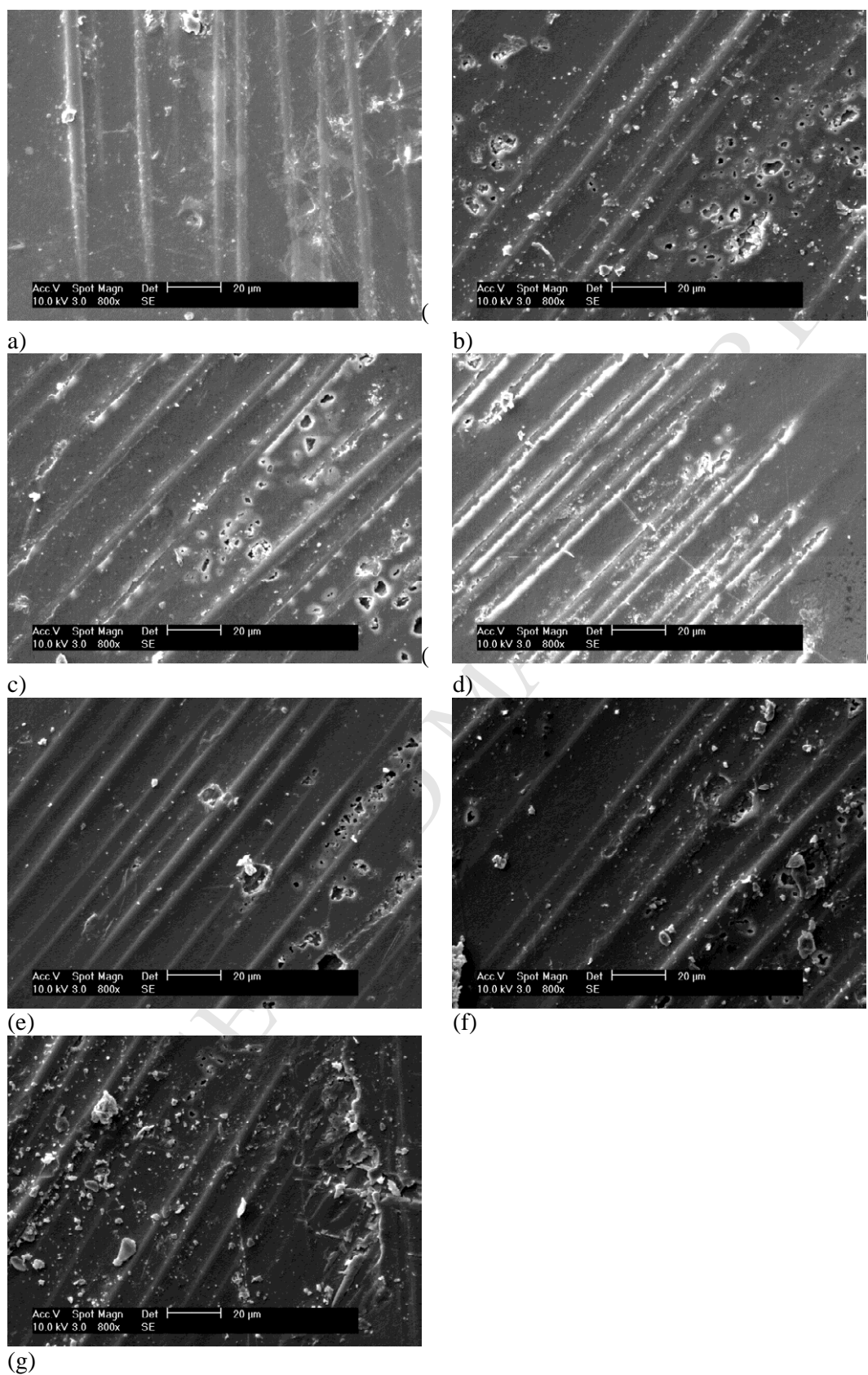


Figure 4 – SEM pictures for: a) Control samples, b) Samples exposed to NaOH during 12 days; c) Samples exposed to NaOH during 24 days; d) Samples exposed to NaOH

during 36 days; e) Samples exposed to HCl during 12 days; f) Samples exposed to HCl during 24 days; g) Samples exposed to HCl during 36 days.

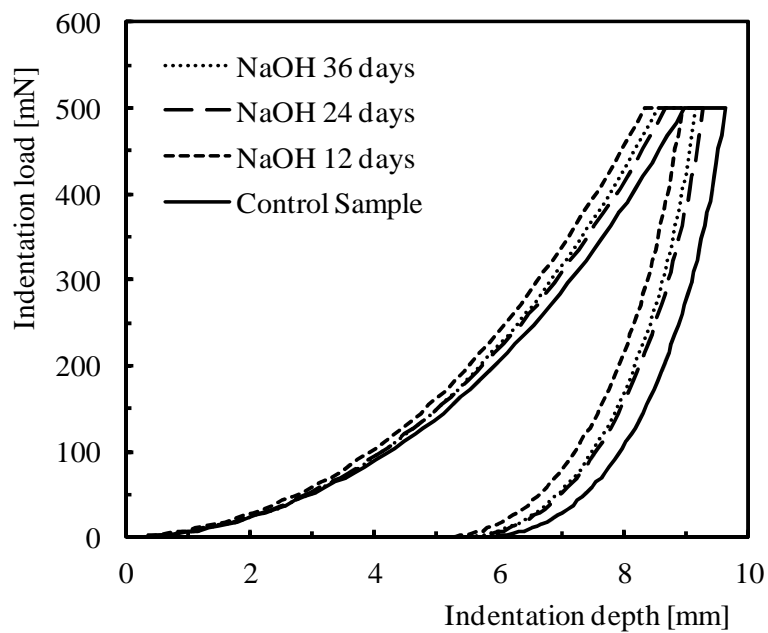


Figure 5 - Schematic representation of the typical load–penetration depth curves.

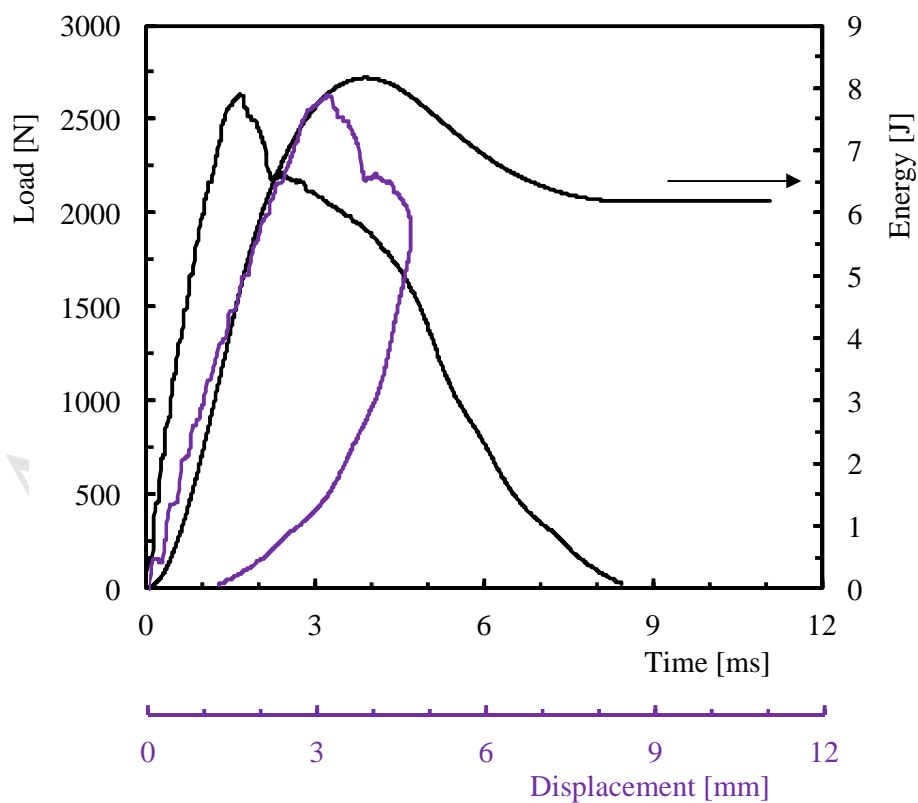




Figure 6 – Typical load-time, load-displacement and energy-time curves for laminates impacted at 8 J before corrosive exposure.

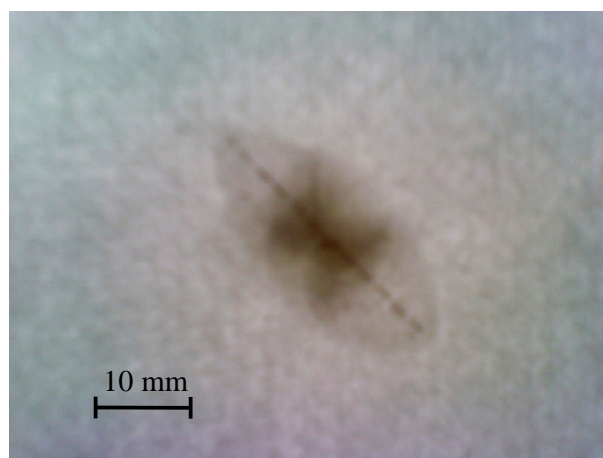


Figure 7 – Typical picture of the damaged laminates impacted at 8 J.

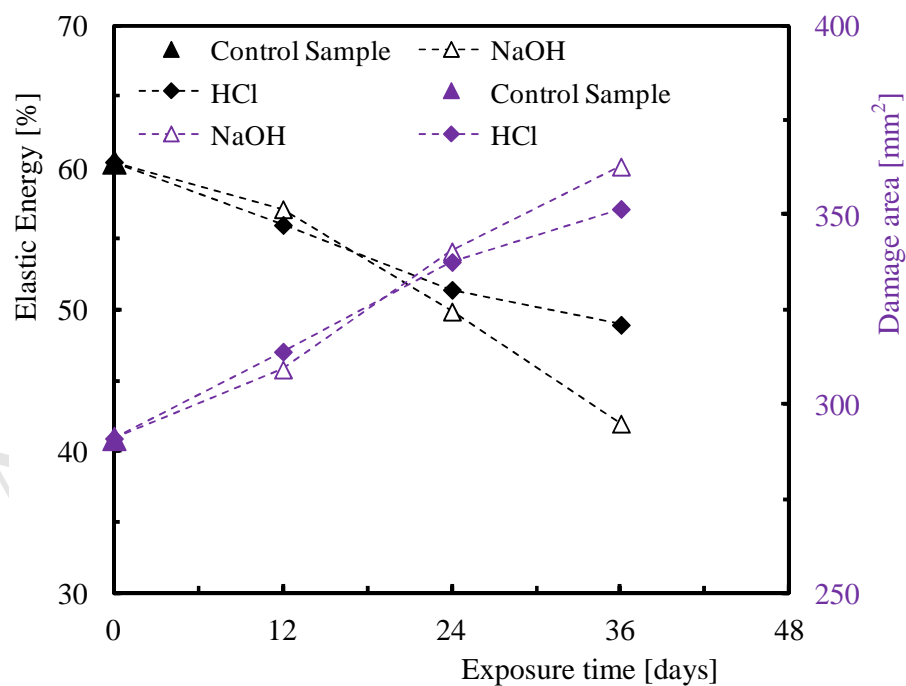
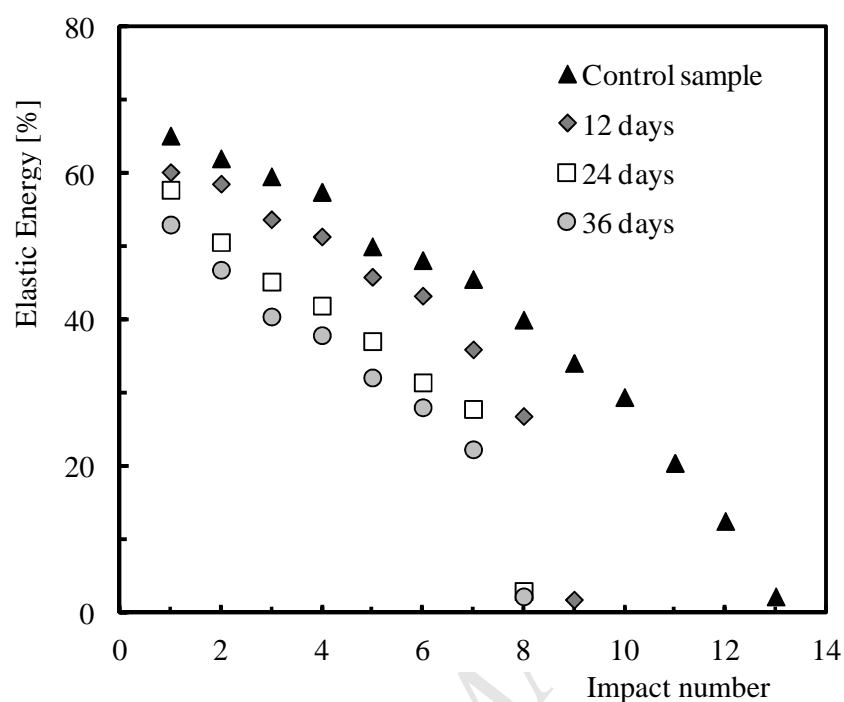
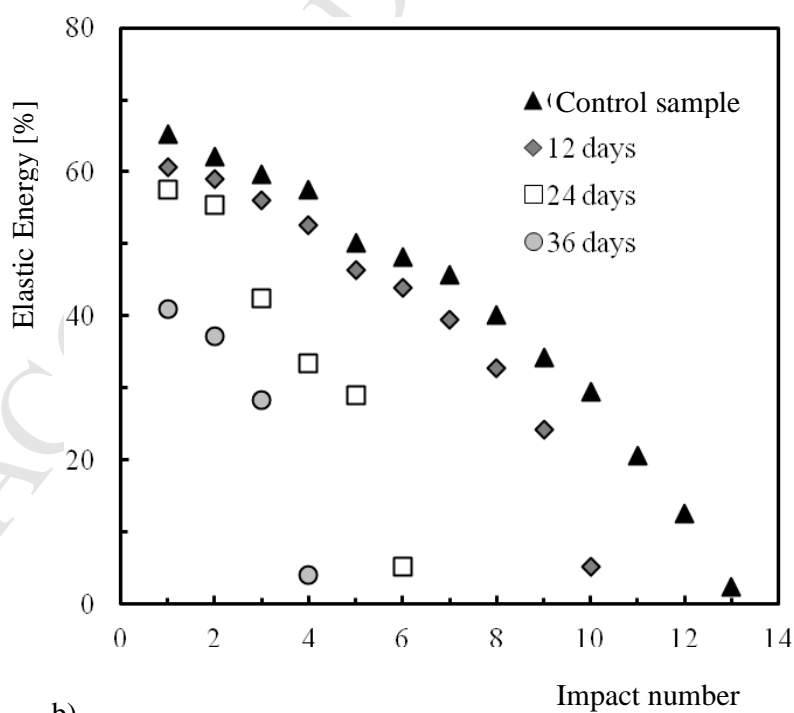


Figure 8 – Effect of the aggressive solutions on elastic energy and damage area after first impact at 4 J.



a)



b)

Figure 9 – Evolution of the elastic energy with the impact numbers for: a) Samples exposed to HCl; b) Samples exposed to NaOH.

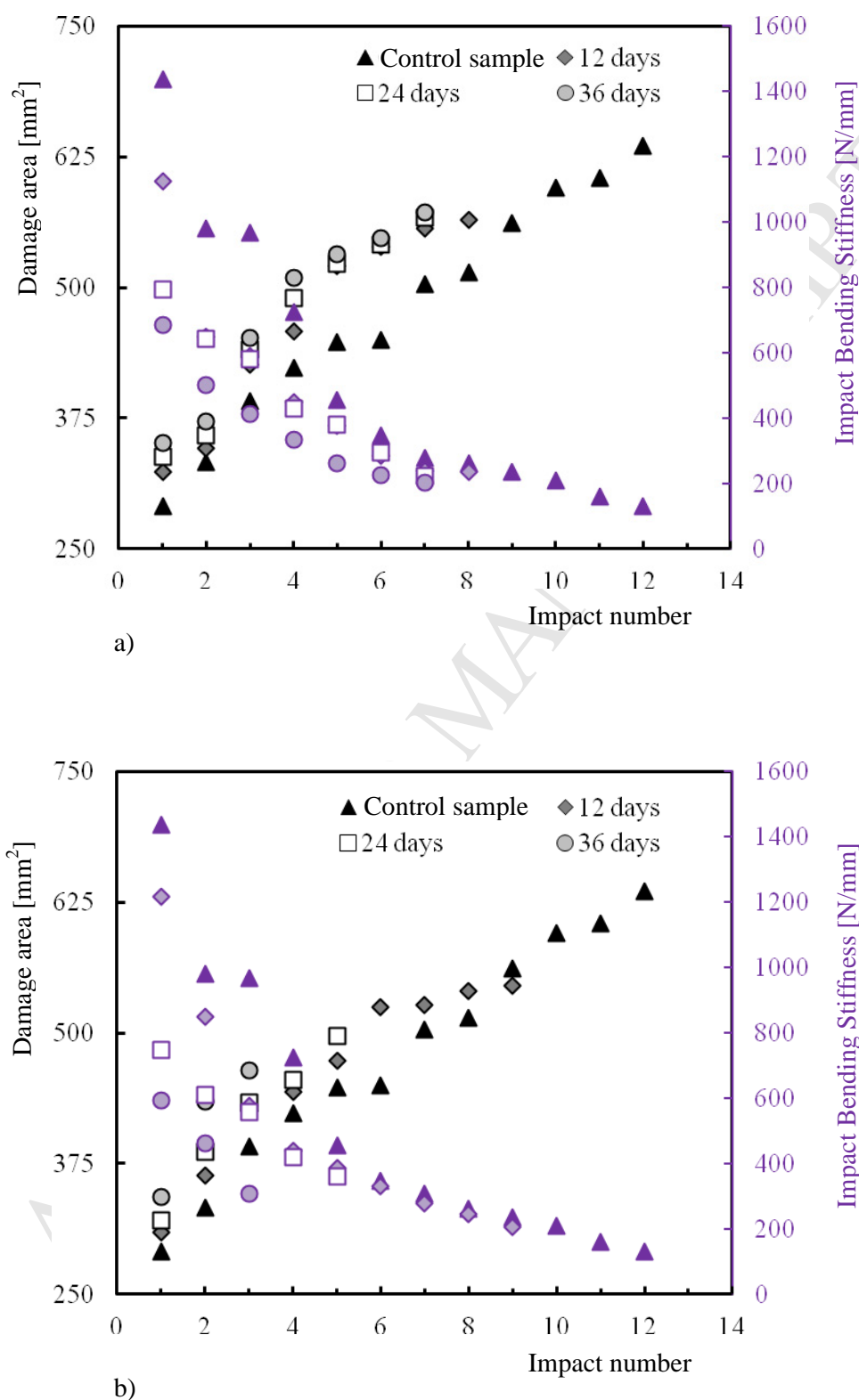


Figure 10 – Evolution of the damage area and impact bending stiffness with the impact numbers for: a) Samples exposed to HCl; b) Samples exposed to NaOH.

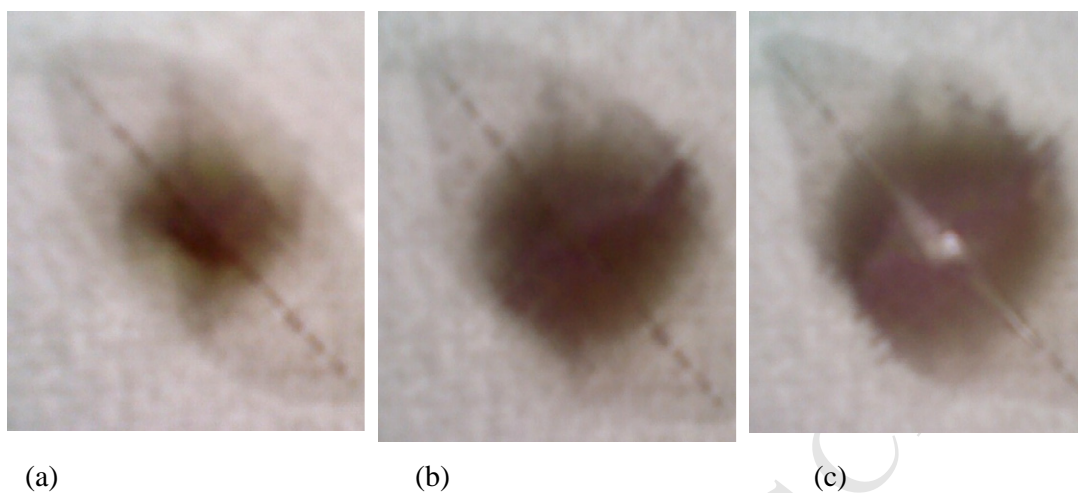


Figure 11 - Typical damages occurred for samples immersed on HCl during 36 days:

(a) 2<sup>nd</sup> Impact; (b) 5<sup>th</sup> Impact; (c) 8<sup>th</sup> Impact.